

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-073538

(43)Date of publication of application : 12.03.2003

(51)Int.Cl.

C08L 67/04
C08G 63/78
C08K 9/04

(21)Application number : 2001-269146

(71)Applicant : TOYOTA CENTRAL RES & DEV LAB INC

(22)Date of filing : 05.09.2001

(72)Inventor : NAKANO MITSURU
OKAMOTO HIROTAKA
TSUKIGASE AZUSA
USUKI ARIMITSU

(54) BIODEGRADABLE RESIN COMPOSITE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a biodegradable resin composite material in which a laminar clay mineral is sufficiently homogeneously dispersed in polylactic acid and which has excellent rigidity and sufficiently high crystallization rate, and to provide a method for producing the same.

SOLUTION: This biodegradable resin composite material is characterized by comprising the polylactic acid and a laminar clay mineral organized with a hydroxyl group-having organic onium salt and bound to the polylactic acid through the hydroxyl group of the organic onium salt.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application converted
registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of
rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Biodegradability resin composite material characterized by containing polylactic acid and the stratified clay mineral which it was made organic by the organic onium salt which has a hydroxyl group, and was combined with said polylactic acid through the hydroxyl group of this organic onium salt.

[Claim 2] Biodegradability resin composite material according to claim 1 characterized by the carbon number of the organic onium salt which has said hydroxyl group being six or more.

[Claim 3] Resin composite material according to claim 1 or 2 characterized by making said stratified clay mineral organic further by the organic onium salt which does not have a hydroxyl group.

[Claim 4] The manufacture approach of the biodegradability resin composite material which carries out melting kneading of the stratified clay mineral and polylactic acid which are obtained to a chemically-modified [which makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, and a chemically-modified [said / organic] degree, and is characterized by including the melting kneading process of making the hydroxyl group of said organic onium salt, and the end carboxyl group of said polylactic acid reacting.

[Claim 5] A chemically-modified [which makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, The stratified clay mineral obtained to a chemically-modified [said / organic] degree, L-lactic acid and D-lactic acid, L-lactide, At least one sort of polymerization nature monomers chosen from the group which consists of a D-lactide and a meso-lactide are mixed. The manufacture approach of the biodegradability resin composite material characterized by including the polymerization process which carries out the polymerization of said polymerization nature monomer by making the hydroxyl group of said organic onium salt into a reacting point, and makes polylactic acid generate.

[Claim 6] The manufacture approach of a biodegradability resin composite material according to claim 4 or 5 characterized by the carbon number of the organic onium salt which has said hydroxyl group being six or more.

[Claim 7] The manufacture approach of a biodegradability resin composite material given in any 1 term of the claims 4-6 characterized by making said stratified clay mineral organic further to a chemically-modified [said / organic] degree by the organic onium salt which does not have a hydroxyl group.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the biodegradability resin composite material containing polylactic acid and a stratified clay mineral, and its manufacture approach in detail about biodegradability resin composite material and its manufacture approach.

[0002]

[Description of the Prior Art] Conventionally, it is known that polylactic acid shows the property decomposed by work of a microorganism and an enzyme and the so-called biodegradability. And the biodegradability resin composite material which added the stratified clay mineral made organic by the organic-ized agent for the purpose of improvement in engine performance, such as a biodegradation rate of polylactic acid, or rigidity and a crystallization rate, to polylactic acid is proposed.

[0003] For example, the sustained-release fertilizer which controlled the rate of dissolution of fertilizer using the coat ingredient containing lactic-acid system polyester and bloating tendency inorganic fillers, such as polylactic acid, is indicated by JP,2000-256087,A, and the stratified silicate by which swelling was carried out with 12-amino-dodecanoic-acid ammonium salt etc. is illustrated as a bloating tendency inorganic filler.

[0004]

[Problem(s) to be Solved by the Invention] However, even if it was the above-mentioned conventional biodegradability resin composite material, it could not say that the distributed homogeneity of a stratified clay mineral was not necessarily enough into polylactic acid, and the improvement effectiveness of rigidity or a crystallization rate by addition of a stratified clay mineral was not enough.

[0005] This invention is made in view of the technical problem which the above-mentioned conventional technique has, and the stratified clay mineral is fully distributing to homogeneity in polylactic acid, and it aims at offering the biodegradability resin composite material which has the outstanding rigidity and a crystallization rate high enough, and its manufacture approach.

[0006]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned object should be attained, this invention persons add the stratified clay mineral made organic by the organic onium salt which has a hydroxyl group to polylactic acid, and came to complete a header and this invention for the above-mentioned technical problem being solved by combining polylactic acid and a stratified clay mineral through the hydroxyl group of organic onium salt.

[0007] That is, biodegradability resin composite material of this invention is characterized by containing polylactic acid and the stratified clay mineral which it was made organic by the organic onium salt which has a hydroxyl group, and was combined with said polylactic acid through the hydroxyl group of this organic onium salt.

[0008] Since polylactic acid is stably held between the layers of the stratified clay mineral which was able to be opened by organic onium salt by making a stratified clay mineral organic by the organic onium salt which has a hydroxyl group, and combining polylactic acid and a stratified clay mineral through the hydroxyl group of this organic onium salt, homogeneity can be made to fully distribute a stratified clay mineral in polylactic acid in the resin composite material of this invention. Consequently, it becomes possible to attain the outstanding rigidity and a crystallization rate high enough.

[0009] Moreover, the 1st manufacture approach of the biodegradability resin composite material of this invention carries out melting kneading of the stratified clay mineral and polylactic acid which are obtained to a chemically-modified [which makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, and a chemically-modified [said / organic] degree, and is characterized by including the melting kneading process of making the hydroxyl group of said organic onium salt, and the end carboxyl group of said polylactic acid reacting.

[0010] Moreover, the 2nd manufacture approach of the biodegradability resin composite material of this invention A chemically-modified [which makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, The stratified clay mineral obtained to a chemically-modified [said / organic] degree, L-lactic acid and D-lactic acid, L-lactide, It is characterized by including the polymerization process which at least one sort of polymerization nature monomers chosen from the group which consists of a D-lactide and a meso-lactide are mixed [process], carries out the polymerization of said polymerization nature monomer by making the hydroxyl group of said organic onium salt into a reacting point, and makes polylactic acid generate.

[0011] Each of the 1st of this invention and 2nd manufacture approach makes association through the hydroxyl group of organic onium salt form between polylactic acid and a stratified clay mineral, and thereby, the stratified clay mineral is fully distributed by homogeneity in polylactic acid, and it can obtain efficiently and certainly the biodegradability resin of this invention which has the outstanding rigidity and a crystallization rate high enough.

[0012] In this invention, it is desirable that the carbon number of the organic onium salt which has said hydroxyl group is six or more. If with a carbon numbers of six or more which have a hydroxyl group organic onium salt is used, since the distance between layers of a stratified clay mineral will be spread more by the organic onium salt concerned, the distributed homogeneity of the stratified clay mineral in polylactic acid is raised, and it is in the inclination the rigidity of biodegradability resin composite material and whose crystallization rate improve.

[0013] Moreover, in this invention, it is desirable that said stratified clay mineral is further made organic by the organic onium salt which does not have a hydroxyl group. Especially the technique of being able to increase the addition, maintaining the distributed homogeneity of a stratified clay mineral excellently, and using organic onium salt together in this way is effective in the 2nd manufacture approach of this invention by using together the organic onium salt which has a hydroxyl group, and the organic onium salt which does not have a hydroxyl group. Moreover, since the molecular weight of the polylactic acid generated by choosing suitably

the content ratio of these two organic onium salt can be adjusted when carrying out the polymerization of the polymerization nature monomer by making the hydroxyl group of organic onium salt into a reacting point like the 2nd manufacture approach of above-mentioned this invention, the addition of a stratified clay mineral can be increased, without reducing the molecular weight of polylactic acid. The biodegradability resin composite material containing such a stratified clay mineral can be obtained by making it organic further by the organic onium salt which does not have a hydroxyl group to a chemically-modified [concerning the 1st of this invention, or the 2nd manufacture approach / organic] degree.

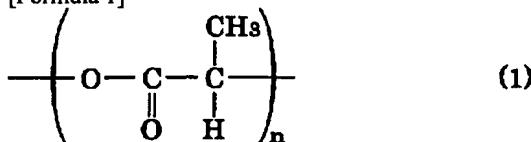
[0014]

[Embodiment of the Invention] Hereafter, the suitable operation gestalt of this invention is explained to a detail.

[0015] Biodegradability resin composite material of this invention is made organic by polylactic acid and the organic onium salt which has a hydroxyl group, and contains the stratified clay mineral combined with said polylactic acid through the hydroxyl group of this organic onium salt. In addition, in this invention, no polylactic acid contained in biodegradability resin composite material needs to combine with the stratified clay mineral through the hydroxyl group of organic onium salt, and those parts should just join together.

[0016] The polylactic acid concerning this invention is following general formula (1): [0017].

[Formula 1]



It is the polymer which has the repeat unit expressed with (n expresses an integer among a formula). Although especially the average molecular weight of the polylactic acid concerned is not restricted, it is desirable that it is 5,000-1,000,000. When it is in the inclination for the average molecular weight of polylactic acid to become insufficient [machine physical properties, such as reinforcement and an elastic modulus,] for it to be said under lower limit and said upper limit is exceeded, it is in the inclination for a fluidity to fall remarkably in the case of shaping.

[0018] Moreover, especially the polymerization method of polylactic acid may not be restricted, but the direct polymerization of L-lactic acid and D-lactic acid is sufficient as it, and it may be the ring opening polymerization of L-lactide which is the annular dimer of a lactic acid, D-lactide, and a meso-lactide. Furthermore, although an optical isomer exists in the polylactic acid obtained using these polymerization nature monomers, you may be any of D-object, L-object, and DL-object, and two or more sorts of mixture of these is sufficient.

[0019] In addition, although association through the hydroxyl group of organic onium salt is formed between stratified clay minerals at the end of polylactic acid so that it may mention later, the polymerization of other polymerization nature monomers, such as glycolide and a caprolactone, is further carried out to the other end, and it is good for it also as a copolymer. As for the polymerization chain by other polymerization nature monomers of these, it is desirable that it is less than [20mol%] on the basis of the whole copolymer.

[0020] Although not restricted especially as a stratified clay mineral concerning this invention, specifically, micas, such as vermiculite group; TENIO lights, such as kaolinite group; JIOKUTAHEDORARU vermiculites, such as smectite group; kaolinites, such as a montmorillonite, beidellite, saponite, and hectorite, and halloysite, and a trio KUTAHEDORARU vermiculite, a tetra-silicic mica, muscovite, an illite, a sericite, a FUROGO cutting tool, and biotite, etc. are mentioned. These stratified clay minerals may be natural minerals, and may be synthetic minerals by hydrothermal synthesis, scorification, a solid phase technique, etc. Moreover, in this invention, one sort in the above-mentioned stratified clay mineral may be used independently, and you may use combining two or more sorts. Moreover, as for the cation exchange capacity of a stratified clay mineral, it is desirable that they are 30-300meq / 100g.

[0021] The organic onium salt which has a hydroxyl group concerning this invention says the compound which the hydroxyl group combined with the organic radical in onium salt, such as organic ammonium salt, organic phosphonium salt, organic pyridinium salt, and organic sulfonium salt, and while making a stratified clay mineral organic and extending the distance between the layer, polylactic acid and a stratified clay mineral are made to combine through a hydroxyl group. In addition, it sets to this invention and organicization means adsorbing and/or combining the organic substance between the layers of a stratified clay mineral, and/or with a front face by the physical and chemical approach (preferably the chemical approach).

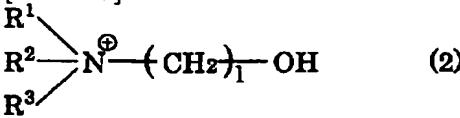
[0022] Although it will not be restricted as organic onium salt which has a hydroxyl group concerning this invention especially if it has a hydroxyl group, as for the carbon number, it is desirable that it is six or more. Distance between layers of a stratified clay mineral cannot fully extend that the carbon number of the organic onium salt concerned is less than six, but it is in the inclination it to become difficult to distribute a stratified clay mineral to homogeneity in polylactic acid.

[0023] As for the content of the organic onium salt which has a hydroxyl group, it is desirable that it is the 10 - 150 weight section to the stratified clay mineral 100 weight section, and it is more desirable that it is the 20 - 100 weight section. Distance between layers of a stratified clay mineral cannot fully extend that the content of the organic onium salt concerned is said under lower limit, but when it is in the inclination which becomes difficult to make homogeneity distribute a stratified clay mineral in polylactic acid and it exceeds another side and said upper limit, it is in the inclination for the amount of the organic onium salt introduced by physical adsorption to increase, and for the physical properties of resin composite material to be spoiled (for example, plasticization).

[0024] As organic onium salt which has the hydroxyl group preferably used by this invention, the organic ammonium salt expressed with the following general formula (2) or (3) is illustrated. One sort may be independently used for such organic ammonium salt, and it may use both together.

[0025]

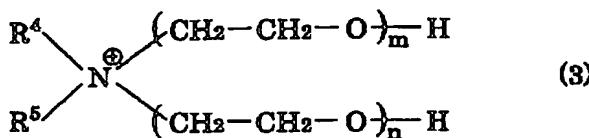
[Formula 2]



[— among the formula, even if R1, R2, and R3 are the same, you may differ, and a hydrogen atom or an alkyl group is expressed, respectively, and 1 expresses the integer of 6-20.]

[0026]

[Formula 3]



[-- among the formula, even if R4 and R5 are the same, you may differ, a hydrogen atom or an alkyl group is expressed, respectively, even if m and n are the same, they may differ from each other, and the carbon number of the sum total of R4 and R5 is six or more, and they express the integer of 1-20.]

[0027] R1, R2, or R3 </SUP> expresses a hydrogen atom or an alkyl group among the above-mentioned general formula (2). As this alkyl group, specifically A methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, sec-butyl, tert-butyl, A straight chain or a branched-chain pentyl radical, a straight chain or a branched-chain hexyl group, a straight chain, or a branched-chain heptyl radical, A straight chain or a branched-chain octyl radical, a straight chain or a branched-chain nonyl radical, a straight chain, or a branched-chain decyl group, Although a straight chain or a branched-chain undecyl radical, a straight chain or the branched-chain dodecyl, a straight chain or a branched-chain tridecyl radical, a straight chain or a branched-chain tetradecyl radical, a straight chain or a branched-chain pentadecyl group, a straight chain, or a branched-chain octadecyl radical is mentioned As for the carbon number of the alkyl group concerned, it is desirable that it is 1-4. When the carbon number of an alkyl group exceeds said upper limit, it is in the inclination for composition of organic onium salt to become difficult.

[0028] moreover, the inside of the above-mentioned general formula (2) and l – the polymerization degree of a methylene group (-CH2-) – expressing – 6-20 – it is the integer of 8-18 preferably. When l is less than six, the distance between layers of a stratified clay mineral does not fully spread, but it is in the inclination for a stratified clay mineral to become is hard to be distributed in polylactic acid in homogeneity. On the other hand, when l exceeds 20, it is in the inclination for composition of organic onium salt to become difficult.

[0029] Moreover, R4 and R5 express a hydrogen atom or an alkyl group among the above-mentioned general formula (3). The alkyl group illustrated as this alkyl group in the explanation of R1, R2, and R3 in a general formula (2) is mentioned.

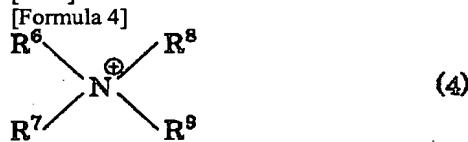
[0030] Although you may differ even if R4 and R5 in a general formula (3) are the same, as for the carbon number of those sum totals, it is desirable that it is six or more, and it is more desirable that it is eight or more. The distance between layers of a stratified clay mineral does not fully spread that the carbon number of the sum total of R4 and R5 is less than six, but it is in the inclination for a stratified clay mineral to become is hard to be distributed in polylactic acid in homogeneity. For example, R4 is preferably used as a compound with which the compound whose R5 is the compound whose R5 is the dodecyl in a hydrogen atom, and whose R4 is an octadecyl radical in a methyl group, and the compound R4 and whose R5 are octadecyl radicals fill the above-mentioned conditions.

[0031] moreover, the inside of the above-mentioned general formula (3), and m and n – the polymerization degree of an oxyethylene radical (-CH2CH2O-) – expressing – 1-20 – desirable – 1-10 – it is the integer of 1-5 more preferably, and is 1 especially preferably. When m or n exceeds 20, it is in the inclination for the hydrophilic property of a stratified clay mineral to become high superfluously, and for adjustment to become difficult. In addition, even if m and n are the same, they may differ.

[0032] In this invention, it is desirable to use the stratified clay mineral further made organic by the organic onium salt which does not have a hydroxyl group in addition to the organic onium salt which has a hydroxyl group. Thus, especially the technique of being able to increase the addition, maintaining the distributed homogeneity of a stratified clay mineral excellently, and using organic onium salt together in this way is effective in the 2nd manufacture approach of this invention by using together the organic onium salt which has a hydroxyl group, and the organic onium salt which does not have a hydroxyl group. Moreover, since the molecular weight of the polylactic acid generated by choosing suitably the content ratio of these two organic onium salt can be adjusted when carrying out the polymerization of the polymerization nature monomer by making the hydroxyl group of organic onium salt into a reacting point like the 2nd manufacture approach of this invention, the addition of a stratified clay mineral can be increased, without reducing the molecular weight of polylactic acid.

[0033] As organic onium salt which does not have the hydroxyl group preferably used in this invention, the organic ammonium salt expressed with the following general formula (4) can be illustrated.

[0034]



[-- among the formula, even if R6, R7, R8, and R9 are the same, you may differ, and a hydrogen atom or an alkyl group is expressed, respectively, and the carbon number of the sum total of R6, R7, R8, and R9 is six or more.]

[0035] R6, R7, R8, and R9 express a hydrogen atom or an alkyl group among the above-mentioned general formula (4), respectively. The alkyl group illustrated as this alkyl group in the explanation of R1, R2, and R3 in a general formula (2) is mentioned.

[0036] Among the above-mentioned general formula (4), the carbon number of the sum total of R6, R7, R8, and R9 is six or more, and is eight or more preferably. It becomes difficult to extend the distance between layers of a stratified clay mineral further by organicization by the organic onium salt as the carbon number of the sum total of R6, R7, R8, and R9 is less than six, and the dispersion effect to the polylactic acid of a stratified clay mineral becomes is hard to be acquired.

[0037] Moreover, in this invention, N (nitrogen atom) in the above-mentioned general formula (4) can also use the organic phosphonium salt permuted by P (Lynn atom).

[0038] When using together the organic onium salt which has a hydroxyl group, and the organic onium salt which does not have a hydroxyl group, it is desirable that it is more than 5mol% on the basis of the organic onium salt whole quantity, as for the blending ratio of coal of organic onium salt which has a hydroxyl group, it is more desirable that it is more than 10mol%, and it is still more desirable that it is more than 15mol%. It is in the inclination as for which becomes inadequate [compatibility with polylactic acid or its polymerization nature monomer (a lactic acid, lactide)] for the blending ratio of coal of organic onium salt which has a hydroxyl group to be less than [5mol%], and these become are hard to be held between the layers of a stratified compound stably.

[0039] In the biodegradability resin composite material of this invention, the latter is 0.5 - 30 weight section preferably to the former 100 weight section, and the content ratio of polylactic acid and the stratified clay mineral made organic is 1 - 20 weight section more preferably. When the content of a stratified clay mineral is in the inclination which becomes inadequate [extent of improvement in

rigidity and a crystallization rate by it being said under lower limit] and exceeds another side and said upper limit, it is in the inclination for it to become impossible for polylactic acid to form a continuation layer, and there is a possibility that the rigidity of biodegradability resin composite material may fall.

[0040] Moreover, as for the distance between layers of the stratified compound contained in the biodegradability resin composite material of this invention, it is desirable that it is 5nm or more on the basis of the mean distance between the centers of gravity of each class, and it is more desirable that it is 10nm or more. It is in the inclination for the distance between layers of a stratified compound to become inadequate [the dispersibility of polylactic acid] for it to be less than 5nm.

[0041] Next, the 1st of the biodegradability resin composite material of this invention and the 2nd manufacture approach are explained.

[0042] The 1st manufacture approach of this invention carries out melting kneading of the stratified clay mineral and polylactic acid which are obtained to a chemically-modified [which makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, and a chemically-modified [organic] degree, and includes the melting kneading process of making the hydroxyl group of organic onium salt, and the end carboxyl group of polylactic acid reacting.

[0043] A chemically-modified [organic] degree can be performed by the approach currently indicated by for example, these people at the patent No. 2627194 official report. That is, organic-ization of a stratified clay mineral can be performed by carrying out the ion exchange by the organic onium ion (for example, setting to organic ammonium salt organic ammonium ion) which produces the inorganic ion in a stratified clay mineral from the organic onium salt which has a hydroxyl group.

[0044] When more specifically using the organic ammonium salt which has a hydroxyl group, organic-ization can be performed by the following approaches. That is, when using a massive stratified clay mineral, first, a ball mill etc. grinds this and it is fine-particles-sized. Subsequently, these fine particles are underwater distributed using a mixer etc., and the water distribution object of a stratified clay mineral is obtained. Apart from this, acids, such as an organic amine which has a hydroxyl group, and a hydrochloric acid, are added to water, and the water solution of the organic ammonium salt which has a hydroxyl group is adjusted. By adding this water solution to the water distribution object of the above-mentioned stratified clay mineral, and mixing up, the ion exchange of the inorganic ion in a stratified clay mineral is carried out by the organic ammonium ion which has the hydroxyl group produced from organic ammonium salt. The stratified clay mineral made organic can be obtained by removing water from this mixture.

[0045] As a dispersion-medium object of organic ammonium salt or a stratified clay mineral, the mixture of these and water can be used for a methanol, ethanol, propanol, isopropanol, ethylene glycol and such mixture, and a list besides water.

[0046] Although a stratified clay mineral may be further made organic by the organic onium salt (for example, organic ammonium salt expressed with the above-mentioned general formula (4)) which does not have a hydroxyl group to a chemically-modified [this / organic] degree, even if it does not perform share opportunity-ization by two sorts of these organic onium salt, the addition can be increased by the 1st manufacture approach, maintaining the distributed homogeneity of a stratified clay mineral excellently. In addition, organic-ization by the organic onium salt which does not have a hydroxyl group may be performed simultaneously with organic-izing by the organic onium salt which has a hydroxyl group, and after organic-izing by the organic onium salt which has a hydroxyl group, it may be performed.

[0047] Next, in a melting kneading process, the biodegradability resin constituent of this invention is obtained by carrying out melting kneading of the stratified clay mineral and polylactic acid which are obtained to a chemically-modified [organic] degree, and making the hydroxyl group of organic onium salt, and the end carboxyl group of polylactic acid react.

[0048] Although it will not be restricted especially if a reaction of the hydroxyl group of organic onium salt and the end carboxyl group of polylactic acid is possible for the temperature in a kneading process, it is 150-250 degrees C preferably. It is in the inclination which the temperature concerned becomes inadequate [melting of polylactic acid] for it to be said under lower limit, and becomes that it is hard to make homogeneity distribute a stratified clay mineral in polylactic acid. Moreover, when the temperature concerned exceeds said upper limit, it is in the inclination for the molecular weight of polylactic acid to fall and for the physical properties of resin composite material to be spoiled (for example, plasticization).

[0049] Moreover, it is desirable to carry out according to the approach currently indicated by these people at the international disclosure WO 99/No. 50340 official report in the case of a kneading process. Namely, a 2 shaft kneading machine equipped with the screw which can add high resin reduced pressure, the quantity total amount of shear, and high shear energy is used. 5x10⁴Pa or more and maximum 1x10⁵Pa, [the average of resin reduced pressure] The total amount of shear can carry out micro-disperse of the stratified clay mineral to homogeneity into polylactic acid by carrying out melting kneading of the stratified clay mineral and polylactic acid which were made organic under the conditions 105-107, and whose total shear energy are 1010-1014Pa.

[0050] A chemically-modified [to which the 2nd manufacture approach of this invention makes a stratified clay mineral organic by the organic onium salt which has a hydroxyl group / organic] degree, The stratified clay mineral obtained to a chemically-modified [organic] degree, L-lactic acid and D-lactic acid, L-lactide, At least one sort of polymerization nature monomers chosen from the group which consists of a D-lactide and a meso-lactide are mixed, and the polymerization process which carries out the polymerization of said polymerization nature monomer by making the hydroxyl group of said organic onium salt into a reacting point, and makes polylactic acid generate is included.

[0051] A chemically-modified [concerning the 2nd manufacture approach / organic] degree can be carried out to the 1st above-mentioned manufacture approach like a chemically-modified [this / organic] degree. Moreover, it is desirable to make a stratified clay mineral organic further by the organic onium salt (for example, organic ammonium salt expressed with the above-mentioned general formula (4)) which does not have a hydroxyl group to a chemically-modified [concerning the 2nd manufacture approach / organic] degree. Thereby, the addition can be increased in the polymerization process mentioned later, maintaining the distributed homogeneity of a stratified clay mineral excellently. Furthermore, since the molecular weight of the polylactic acid which controls the abundance of the hydroxyl group between the layers of a stratified clay mineral and/or in a front face, and is generated can be adjusted by choosing suitably the content ratio of these two organic onium salt, the addition of a stratified clay mineral can be increased, without reducing the molecular weight of polylactic acid. In addition, organic-ization by the organic onium salt which does not have a hydroxyl group may be performed simultaneously with organic-izing by the organic onium salt which has a hydroxyl group, and after organic-izing by the organic onium salt which has a hydroxyl group, it may be performed.

[0052] Next, in a polymerization process, polylactic acid generates by mixing at least one sort of polymerization nature monomers chosen from the stratified clay mineral obtained to a chemically-modified [organic] degree, and the group which consists of L-lactic acid, D-lactic acid, an L-lactide, and a D-lactide, and carrying out the polymerization of said polymerization nature monomer by making the hydroxyl group of said organic onium salt into a reacting point. Here, in using L-lactic acid and/or D-lactic acid, polylactic acid generates according to these direct polycondensations, and in using another side, L-lactide, and/or D-lactide, polylactic acid generates by such ring opening polymerization. These polymerizations may be performed using a predetermined catalyst and may be performed under a non-catalyst. As a catalyst, octylic acid tin, tin chloride, a zinc chloride, a lead oxide, lead carbonate, a titanium

chloride, alkoxy titanium, a germanium dioxide, a zirconium dioxide, etc. are mentioned, and, as for the amount used, specifically, it is desirable that it is 0.001 - 1 weight section to the polymerization nature monomer 100 weight section. Moreover, as for the reaction temperature in a polymerization process, it is desirable that it is 100-200 degrees C.

[0053] Thus, each of the 1st of this invention and 2nd manufacture approach makes association through the hydroxyl group of organic onium salt form between polylactic acid and a stratified clay mineral, and thereby, a stratified clay mineral is fully distributed by homogeneity in polylactic acid, and it can obtain efficiently and certainly the biodegradability resin of this invention which has the outstanding rigidity and crystal acceleration high enough.

[0054]

[Example] Hereafter, although this invention is explained still more concretely based on an example and the example of a comparison, this invention is not limited to the following examples at all.

[0055] 5000ml of 80-degree C water was made to distribute example 1 (organic-izing of stratified clay mineral) sodium mold montmorillonite (KUNIPIAF made from KUNIMINE mining, cation-exchange-capacity:115meq / 100g) 100g, on the other hand, after dissolving dihydroxyethyl MECHIRUSUTEARIRU ammonium bromide 59.2g in 2000ml of 80-degree C water, both were mixed and organic-ization of a montmorillonite was performed. 80-degree C water washed the obtained organic-ized montmorillonite (henceforth 18(OH)2-Mont) 3 times, and this was ground after freeze-drying. The residue for inorganic of 18(OH)2-Mont calculated by the *** method was 63%.

[0056] (Kneading with a stratified clay mineral and polylactic acid) Melting kneading of the mixture which added 18(OH)2-Mont 3% of the weight with the inorganic part reduced property to polylactic resin (Shimadzu Lacty # 9030) was carried out using the twin screw extruder (Japan Steel Works TEX30alpha) equipped with a screw by screw-speed 300rpm, the resin temperature of 200 degrees C, and resin speed-of-supply 5 kg/h, and the target resin composite material was obtained. After extruding the obtained resin composite material in the shape of a strand, it quenched with water and considered as the pellet with the strand cutter.

[0057] (Assessment of a distributed condition) The above-mentioned pellet was started with the microtome and the ultrathin section was produced. x: in which the stratified clay mineral in the condition that the **:2-3 layer to which this is observed with a transmission electron microscope (JEOL JOEL- 200 CX), and the following criteria: O: stratified clay minerals are carrying out micro-disperse of the distributed condition of a stratified clay mineral for every monolayer mostly condensed is accepted 50% or more -- most stratified clay minerals distribute, where dozens of or more layers are condensed -- *** -- it based and evaluated. The obtained result is shown in a table 1.

[0058] (Rigid assessment) Injection molding of the above-mentioned resin composite material was performed using the injection molding machine (NISSEI PLASTIC INDUSTRIAL PS 40E2 ASE) and FS75 mold, and the dumbbell mold test piece for tensile test was obtained. This test piece is used and it is ASTM. The tensile test was performed according to D638M, and tensile strength, elongation after fracture, and an elastic modulus were evaluated. Moreover, ASTM The Izod impact test was performed according to D256. The obtained result is shown in a table 1.

[0059] (Measurement of crystallization time amount) Crystallization time amount was measured with the DSC measuring device (DSC[by PerkinElmer, Inc.]- 7) using the above-mentioned pellet. That is, 0.3mg of samples was paid to the aluminum pan, and time amount after holding for 5 minutes at 200 degrees C, lowering the temperature rapidly, holding and lowering the temperature to 110 degrees C until the endoergic peak of crystallization appears was made into crystallization time amount. The obtained result is shown in a table 1.

[0060] Instead of example 2 dihydroxyethyl methyl stearyl ammonium salt dihydroxyethyl methyl alkyl ammonium salt (the alkyl group of Kao AMITO 102 and the alkyl:palm oil origin --) Presentation : Organic-ization of a montmorillonite is performed using octyl / DESHIRU / dodecyl / tetradecyl / octadecyl / oleyl =7/7/51/19/8/2/6. Except having used the obtained organic-ized montmorillonite (A102-Mont), like the example 1, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 1.

[0061] an example 3 -- 18(OH)2-Mont was first compounded like the example 1. Next, L-lactide 100g, 18(OH)2-Mont3.5g, and octylic acid tin 200mg were put into the reaction container, and it decompressed to 10-2mmHg. Then, temperature was raised gradually, agitating enough and it held at 160 degrees C for 3 hours. The resultant was dissolved in chloroform, it was dropped into the methanol, and isolation purification of the resin composite material was carried out.

[0062] About the obtained resin composite material, crystallization time amount was measured in the distributed condition and the rigid assessment list like the example 1. The obtained result is shown in a table 1.

[0063] Except having used the montmorillonite (11 OH-Mont) made organic by 3 (CH₃C H₂)N+(CH₂)₁₁OHBr- instead of example 418(OH)2-Mont, like the example 3, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 1.

[0064] Except having used the montmorillonite (OH/C18-Mont) made organic with the mixture (mole ratio 7:3) of dihydroxyethyl stearyl ammonium salt and trimethyl stearyl ammonium salt instead of example 518(OH)2-Mont, like the example 3, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 1.

[0065] Example of comparison 1 polylactic acid was used independently, and rigid assessment and measurement of crystallization time amount were performed like the example 1. The obtained result is shown in a table 2.

[0066] Except having used the montmorillonite (12 COOH-Mont) made organic by 12-amino dodecanoic acid instead of example of comparison 218(OH)2-Mont, like the example 1, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 2.

[0067] Except having used the montmorillonite (C18Me3-Mont) made organic by stearyl trimethylammonium instead of example of comparison 318(OH)2-Mont, like the example 1, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 2.

[0068] Except having used 12 COOH-Mont instead of example of comparison 418(OH)2-Mont, like the example 3, resin composite material was produced and crystallization time amount was measured in the distributed condition and the rigid assessment list. The obtained result is shown in a table 2.

[0069]

[A table 1]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
分散状態	○	○	○	○	○
引張強さ [MPa]	72.4	70.4	71.9	70.8	70.0
引張破断伸び[%]	5.2	5.4	5.1	5.6	4.9
引張弾性率 [GPa]	1.65	1.62	1.64	1.62	1.64
Izod衝撃値 [J/n]	23.8	25.0	24.1	23.5	22.9
結晶化時間[min]	5.3	10.5	5.0	6.1	6.9

[0070]

[A table 2]

	比較例 1	比較例 2	比較例 3	比較例 4
分散状態	-	×	×	△
引張強さ [MPa]	61.2	45.3	58.0	59.5
引張破断伸び[%]	8.4	1.5	2.8	3.1
引張弾性率 [GPa]	1.31	1.52	1.58	1.58
Izod衝撃値 [J/n]	26.6	12.2	18.2	18.8
結晶化時間[min]	54.5	42.2	35.5	32.7

[0071] As shown in a table 1, in the resin composite material of examples 1-5, the stratified clay mineral was all distributing minutely in polylactic acid, and improvement in rigidity and a crystallization rate was accepted compared with the polylactic acid independent (example 1 of a comparison) case.

[0072] On the other hand, as shown in a table 2, in the resin composite material of the examples 2-4 of a comparison, it was distributing in polylactic acid, with the stratified clay mineral condensing, and it only turned out [hard] that it is a weak ingredient.

[0073]

[Effect of the Invention] Since polylactic acid is stably held between the layers of the stratified clay mineral which was able to be opened by organic onium salt by making a stratified clay mineral organic by the organic onium salt which has a hydroxyl group, and combining polylactic acid and a stratified clay mineral through the hydroxyl group of this organic onium salt, homogeneity can be made to fully distribute a stratified clay mineral in polylactic acid in the resin composite material of this invention as explained above. Consequently, it becomes possible to attain the outstanding rigidity and a crystallization rate high enough.

[0074] Moreover, according to the manufacture approach of the resin composite material of this invention, the resin composite material of this invention which has the property which was excellent in this way can be obtained efficiently and certainly.

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-073538
(43)Date of publication of application : 12.03.2003

(51)Int.CI. C08L 67/04
C08G 63/78
C08K 9/04

(21)Application number : 2001-269146 (71)Applicant : TOYOTA CENTRAL RES & DEV LAB INC
(22)Date of filing : 05.09.2001 (72)Inventor : NAKANO MITSURU
OKAMOTO HIROTAKA
TSUKIGASE AZUSA
USUKI ARIMITSU

(54) BIODEGRADABLE RESIN COMPOSITE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a biodegradable resin composite material in which a laminar clay mineral is sufficiently homogeneously dispersed in polylactic acid and which has excellent rigidity and sufficiently high crystallization rate, and to provide a method for producing the same.

SOLUTION: This biodegradable resin composite material is characterized by comprising the polylactic acid and a laminar clay mineral organized with a hydroxyl group-having organic onium salt and bound to the polylactic acid through the hydroxyl group of the organic onium salt.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(19) 日本国特許庁(JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2003-73538

(P2003-73538A)

(43) 公開日 平成15年3月12日 (2003.3.12)

(51) Int. C1. 7 識別記号
C08L 67/04 ZBP
C08G 63/78
C08K 9/04

F I
C08L 67/04 ZBP 4J002
C08G 63/78 4J029
C08K 9/04

審査請求 未請求 請求項の数 7 O L

(全8頁)

(21) 出願番号 特願2001-269146 (P2001-269146)

(71) 出願人 000003609

株式会社豊田中央研究所
愛知県愛知郡長久手町大字長湫字横道41番
地の1

(22) 出願日 平成13年9月5日 (2001.9.5)

(72) 発明者 中野 充

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内

(72) 発明者 岡本 浩孝

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内

(74) 代理人 100088155

弁理士 長谷川 芳樹 (外3名)

最終頁に続く

(54) 【発明の名称】生分解性樹脂複合材料

(57) 【要約】

【課題】 ポリ乳酸中に層状粘土鉱物が十分に均一に分散しており、優れた剛性と十分に高い結晶化速度とを有する生分解性樹脂複合材料及びその製造方法を提供すること。

【解決手段】 本発明の生分解性樹脂複合材料は、ポリ乳酸と、水酸基を有する有機オニウム塩で有機化され、該有機オニウム塩の水酸基を介してポリ乳酸と結合した層状粘土鉱物とを含有することを特徴とする。

【特許請求の範囲】

【請求項1】 ポリ乳酸と、水酸基を有する有機オニウム塩で有機化され、該有機オニウム塩の水酸基を介して前記ポリ乳酸と結合した層状粘土鉱物とを含有することを特徴とする生分解性樹脂複合材料。

【請求項2】 前記水酸基を有する有機オニウム塩の炭素数が6以上であることを特徴とする、請求項1に記載の生分解性樹脂複合材料。

【請求項3】 前記層状粘土鉱物が、水酸基を有さない有機オニウム塩で更に有機化されていることを特徴とする、請求項1又は2に記載の樹脂複合材料。

【請求項4】 水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物とポリ乳酸とを溶融混練し、前記有機オニウム塩の水酸基と前記ポリ乳酸の末端カルボキシル基とを反応させる溶融混練工程とを含むことを特徴とする生分解性樹脂複合材料の製造方法。

【請求項5】 水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と、L-乳酸、D-乳酸、L-ラクチド、D-ラクチド及びmeso-ラクチドからなる群より選ばれる少なくとも1種の重合性单量体とを混合し、前記有機オニウム塩の水酸基を反応点として前記重合性单量体を重合させてポリ乳酸を生成させる重合工程とを含むことを特徴とする生分解性樹脂複合材料の製造方法。

【請求項6】 前記水酸基を有する有機オニウム塩の炭素数が6以上であることを特徴とする、請求項4又は5に記載の生分解性樹脂複合材料の製造方法。

【請求項7】 前記有機化工程において、前記層状粘土鉱物を、水酸基を有さない有機オニウム塩で更に有機化することを特徴とする、請求項4～6のうちのいずれか一項に記載の生分解性樹脂複合材料の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、生分解性樹脂複合材料及びその製造方法に関するものであり、詳しくは、ポリ乳酸と層状粘土鉱物とを含有する生分解性樹脂複合材料及びその製造方法に関するものである。

【0002】

【従来の技術】 従来、ポリ乳酸は、微生物や酵素の働きにより分解する性質、いわゆる生分解性を示すことが知られている。そして、ポリ乳酸の生分解速度、あるいは剛性や結晶化速度といった性能の向上を目的として、有機化剤で有機化された層状粘土鉱物をポリ乳酸に添加した生分解性樹脂複合材料が提案されている。

【0003】 例えば特開2000-256087号公報には、ポリ乳酸等の乳酸系ポリエステルと膨潤性無機フィラーとを含む皮膜材料を用いて肥料の溶出速度を制御した徐放性肥料が開示されており、膨潤性無機フィラー

として、12-アミノドекан酸アンモニウム塩等で膨潤化された層状ケイ酸塩が例示されている。

【0004】

【発明が解決しようとする課題】 しかしながら、上記従来の生分解性樹脂複合材料であっても、ポリ乳酸中に層状粘土鉱物の分散均一性は必ずしも十分とは言えず、層状粘土鉱物の添加による剛性や結晶化速度の向上効果は十分なものではなかった。

【0005】 本発明は、上記従来技術の有する課題に鑑みてなされたものであり、ポリ乳酸中に層状粘土鉱物が十分に均一に分散しており、優れた剛性と十分に高い結晶化速度とを有する生分解性樹脂複合材料及びその製造方法を提供することを目的とする。

【0006】

【課題を解決するための手段】 本発明者らは、上記目的を達成すべく銳意研究を重ねた結果、水酸基を有する有機オニウム塩で有機化された層状粘土鉱物をポリ乳酸に添加し、ポリ乳酸と層状粘土鉱物とを有機オニウム塩の水酸基を介して結合させることによって上記課題が解決されることを見出し、本発明を完成するに至った。

【0007】 すなわち、本発明の生分解性樹脂複合材料は、ポリ乳酸と、水酸基を有する有機オニウム塩で有機化され、該有機オニウム塩の水酸基を介して前記ポリ乳酸と結合した層状粘土鉱物とを含有することを特徴とするものである。

【0008】 本発明の樹脂複合材料では、水酸基を有する有機オニウム塩で層状粘土鉱物を有機化し、該有機オニウム塩の水酸基を介してポリ乳酸と層状粘土鉱物とを結合させることによって、有機オニウム塩により広げられた層状粘土鉱物の層間にポリ乳酸が安定的に保持されるので、層状粘土鉱物をポリ乳酸中に十分に均一に分散させることができる。その結果、優れた剛性と十分に高い結晶化速度とを達成することが可能となる。

【0009】 また、本発明の生分解性樹脂複合材料の第1の製造方法は、水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物とポリ乳酸とを溶融混練し、前記有機オニウム塩の水酸基と前記ポリ乳酸の末端カルボキシル基とを反応させる溶融混練工程とを含むことを特徴とするものである。

【0010】 また、本発明の生分解性樹脂複合材料の第2の製造方法は、水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、前記有機化工程で得られる層状粘土鉱物と、L-乳酸、D-乳酸、L-ラクチド、D-ラクチド及びmeso-ラクチドからなる群より選ばれる少なくとも1種の重合性单量体とを混合し、前記有機オニウム塩の水酸基を反応点として前記重合性单量体を重合させてポリ乳酸を生成させる重合工程とを含むことを特徴とするものである。

【0011】 本発明の第1及び第2の製造方法は、いずれ

もポリ乳酸と層状粘土鉱物との間に有機オニウム塩の水酸基を介した結合を形成させるもので、これにより、層状粘土鉱物がポリ乳酸中に十分に均一に分散されており、優れた剛性と十分に高い結晶化速度とを有する本発明の生分解性樹脂を効率よく且つ確実に得ることができる。

【0012】本発明においては、前記水酸基を有する有機オニウム塩の炭素数が6以上であることが好ましい。水酸基を有する炭素数6以上の有機オニウム塩を用いると、当該有機オニウム塩により層状粘土鉱物の層間距離がより広められるので、ポリ乳酸中における層状粘土鉱物の分散均一性が高められ、生分解性樹脂複合材料の剛性及び結晶化速度が向上する傾向にある。

【0013】また、本発明においては、前記層状粘土鉱物が、水酸基を有さない有機オニウム塩で更に有機化されていることが好ましい。水酸基を有する有機オニウム塩と、水酸基を有さない有機オニウム塩とを併用することによって、層状粘土鉱物の分散均一性を高水準に維持しつつその添加量を増加することができ、このように有機オニウム塩を併用する手法は本発明の第2の製造方法において特に効果的である。また、上記本発明の第2の製造方法のように有機オニウム塩の水酸基を反応点として重合性単量体を重合させる場合には、これら2つの有機オニウム塩の含有比率を適宜選択することによって、生成するポリ乳酸の分子量を調整することができる。ポリ乳酸の分子量を低下させずに層状粘土鉱物の添加量を増加することができる。このような層状粘土鉱物を含有する生分解性樹脂複合材料は、本発明の第1又は第2の製造方法にかかる有機化工程において、水酸基を有さない有機オニウム塩で更に有機化することによって得ることができる。

【0014】

【発明の実施の形態】以下、本発明の好適な実施形態について詳細に説明する。

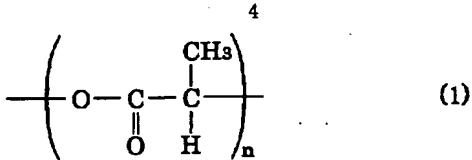
【0015】本発明の生分解性樹脂複合材料は、ポリ乳酸と、水酸基を有する有機オニウム塩で有機化され、該有機オニウム塩の水酸基を介して前記ポリ乳酸と結合した層状粘土鉱物とを含有するものである。なお、本発明においては、生分解性樹脂複合材料に含まれる全てのポリ乳酸が有機オニウム塩の水酸基を介して層状粘土鉱物と結合している必要はなく、それらの一部が結合したものであればよい。

【0016】本発明にかかるポリ乳酸は、下記一般式

(1) :

【0017】

【化1】



(式中、nは整数を表す)で表される繰り返し単位を有するポリマーである。当該ポリ乳酸の平均分子量は特に制限されないが、5,000~1,000,000であることが好ましい。ポリ乳酸の平均分子量が前記下限値未満であると、強度、弾性率等の機械物性が不十分となる傾向にあり、また、前記上限値を超えると、成形の際に流動性が著しく低下する傾向にある。

【0018】また、ポリ乳酸の重合方法は特に制限されず、L-乳酸、D-乳酸の直接重合でもよく、乳酸の環状2量体であるL-ラクチド、D-ラクチド、meso-ラクチドの開環重合であってもよい。更に、これらの重合性単量体を用いて得られるポリ乳酸には光学異性体が存在するが、D-体、L-体、DL-体のいずれであってもよく、またこれらのうちの2種以上の混合物でもよい。

【0019】なお、後述するように、ポリ乳酸の一端には、層状粘土鉱物との間に有機オニウム塩の水酸基を介した結合が形成されるが、他端には、グリコリド、カブロラクトン等の他の重合性単量体を更に重合させて共重合体としてもよい。これらの他の重合性単量体による重合鎖は、共重合体全体を基準として20mol%以下であることが好ましい。

【0020】本発明にかかる層状粘土鉱物としては特に制限されないが、具体的には、モンモリロナイト、パイデライト、サボナイト、ヘクトサイト等のスマクタイト族；カオリナイト、ハロサイト等のカオリナイト族；ジオクタヘドralバーミキュライト、トリオクタヘドralバーミキュライト等のバーミキュライト族；テニオライト、テトラシリシックマイカ、マスコバイト、イライト、セリサイト、フロゴバイト、バイオタイト等のマイカ等が挙げられる。これらの層状粘土鉱物は、天然鉱物であってもよく、水熱合成、溶融法、固相法等による合成鉱物であってもよい。また、本発明では、上記の層状粘土鉱物のうちの1種を単独で用いてもよく、2種以上を組み合わせて用いてもよい。また、層状粘土鉱物の陽イオン交換容量は30~300meq/100gであることが好ましい。

【0021】本発明にかかる水酸基を有する有機オニウム塩とは、有機アンモニウム塩、有機ホスホニウム塩、有機ピリジニウム塩、有機スルホニウム塩等のオニウム塩において有機基に水酸基が結合した化合物をいい、層状粘土鉱物を有機化してその層間距離を広げると共に、水酸基を介してポリ乳酸と層状粘土鉱物とを結合せしめるものである。なお、本発明において有機化とは、有機物を層状粘土鉱物の層間及び/又は表面に物理的、化学

の方法（好ましくは化学的方法）により吸着及び／又は結合させることを意味する。

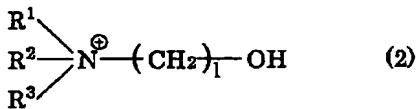
【0022】本発明にかかる水酸基を有する有機オニウム塩としては、水酸基を有するものであれば特に制限されないが、その炭素数は6以上であることが好ましい。当該有機オニウム塩の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広げられず、層状粘土鉱物をポリ乳酸中に均一に分散することが困難となる傾向にある。

【0023】水酸基を有する有機オニウム塩の含有量は、層状粘土鉱物100重量部に対して10～150重量部であることが好ましく、20～100重量部であることがより好ましい。当該有機オニウム塩の含有量が前記下限値未満であると、層状粘土鉱物の層間距離が十分に広げられず、層状粘土鉱物をポリ乳酸中に均一に分散させることが困難となる傾向にあり、他方、前記上限値を超える場合には物理吸着によって導入される有機オニウム塩の量が増加して樹脂複合材料の物性が損なわれる（例えは可塑化）傾向にある。

【0024】本発明で好ましく用いられる水酸基を有する有機オニウム塩として、下記一般式（2）又は（3）で表される有機アンモニウム塩が例示される。これらの有機アンモニウム塩は、1種を単独で用いてもよく、両者を併用してもよい。

【0025】

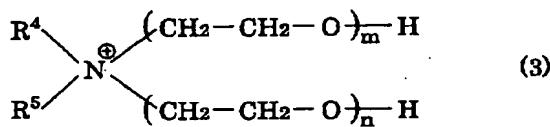
【化2】



【式中、R¹、R²及びR³は同一でも異なっていてもよく、それぞれ水素原子又はアルキル基を表し、1は6～20の整数を表す。】

【0026】

【化3】



【式中、R⁴及びR⁵は同一でも異なっていてもよく、それぞれ水素原子又はアルキル基を表し、R⁴とR⁵との合計の炭素数は6以上であり、m及びnは同一でも異なっていてもよく、1～20の整数を表す。】

【0027】上記一般式（2）中、R¹、R²又はR³は水素原子又はアルキル基を表す。かかるアルキル基としては、具体的には、メチル基、エチル基、n-ブロピル基、i-ブロピル基、n-ブチル基、sec-ブチル基、tert-ブチル基）、直鎖又は分岐鎖状のペンチル基、直鎖又は分岐鎖状のヘキシル基、直鎖又は分岐鎖

状のヘプチル基、直鎖又は分岐鎖状のオクチル基、直鎖又は分岐鎖状のノニル基、直鎖又は分岐鎖状のデシル基、直鎖又は分岐鎖状のウンデシル基、直鎖又は分岐鎖状のドデシル基、直鎖又は分岐鎖状のトリデシル基、直鎖又は分岐鎖状のペンタデシル基、直鎖又は分岐鎖状のオクタデシル基等が挙げられるが、当該アルキル基の炭素数は1～4であることが好ましい。アルキル基の炭素数が前記上限値を超えると有機オニウム塩の合成が困難となる傾向にある。

【0028】また、上記一般式（2）中、1はメチレン基（-CH₂-）の重合度を表し、6～20、好ましくは8～18の整数である。1が6未満の場合、層状粘土鉱物の層間距離が十分に広がらず、層状粘土鉱物がポリ乳酸中に均一に分散されにくくなる傾向にある。他方、1が20を越えると、有機オニウム塩の合成が困難となる傾向にある。

【0029】また、上記一般式（3）中、R⁴及びR⁵は水素原子又はアルキル基を表す。かかるアルキル基としては、一般式（2）中のR¹、R²及びR³の説明において例示されたアルキル基が挙げられる。

【0030】一般式（3）中のR⁴及びR⁵は同一でも異なっていてもよいが、それらの合計の炭素数は、6以上であることが好ましく、8以上であることがより好ましい。R⁴とR⁵との合計の炭素数が6未満であると、層状粘土鉱物の層間距離が十分に広がらず、層状粘土鉱物がポリ乳酸中に均一に分散されにくくなる傾向にある。例えばR⁴が水素原子でR⁵がドデシル基である化合物、R⁴がメチル基でR⁵がオクタデシル基である化合物、R⁴及びR⁵がオクタデシル基である化合物は、上記の条件を満たす化合物として好ましく用いられる。

【0031】また、上記一般式（3）中、m及びnはオキシエチレン基（-CH₂CH₂O-）の重合度を表し、1～20、好ましくは1～10、より好ましくは1～5の整数であり、特に好ましくは1である。m又はnが20を越えると、層状粘土鉱物の親水性が過剰に高くなり、調整が困難となる傾向にある。なお、m及びnは同一でも異なっていてもよい。

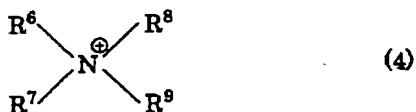
【0032】本発明においては、水酸基を有する有機オニウム塩に加えて、水酸基を有さない有機オニウム塩で更に有機化された層状粘土鉱物を用いることが好ましい。このように水酸基を有する有機オニウム塩と、水酸基を有さない有機オニウム塩とを併用することによって、層状粘土鉱物の分散均一性を高水準に維持しつつその添加量を増加することができ、このように有機オニウム塩を併用する手法は本発明の第2の製造方法において特に効果的である。また、本発明の第2の製造方法のように、有機オニウム塩の水酸基を反応点として重合性单量体を重合させる場合には、これら2つの有機オニウム塩の含有比率を適宜選択することによって、生成するポ

リ乳酸の分子量を調整することができるので、ポリ乳酸の分子量を低下させずに層状粘土鉱物の添加量を増加することができる。

【0033】本発明において好ましく用いられる水酸基を有さない有機オニウム塩としては、下記一般式(4)で表される有機アンモニウム塩を例示することができる。

【0034】

【化4】



【式中、R⁶、R⁷、R⁸及びR⁹は同一でも異なっていてもよく、それぞれ水素原子またはアルキル基を表し、R⁶、R⁷、R⁸及びR⁹の合計の炭素数は6以上である。】

【0035】上記一般式(4)中、R⁶、R⁷、R⁸及びR⁹はそれぞれ水素原子又はアルキル基を表す。かかるアルキル基としては、一般式(2)中のR¹、R²及びR³の説明において例示されたアルキル基が挙げられる。

【0036】上記一般式(4)中、R⁶、R⁷、R⁸及びR⁹の合計の炭素数は6以上であり、好ましくは8以上である。R⁶、R⁷、R⁸及びR⁹の合計の炭素数が6未満であると、その有機オニウム塩での有機化により層状粘土鉱物の層間距離を更に広げることが困難となり、層状粘土鉱物のポリ乳酸への分散効果が得られにくくなる。

【0037】また、本発明では、上記一般式(4)中のN(窒素原子)がP(リン原子)で置換された有機ホスホニウム塩を用いることもできる。

【0038】水酸基を有する有機オニウム塩と水酸基を有さない有機オニウム塩とを併用する場合、水酸基を有する有機オニウム塩の配合割合は、有機オニウム塩全量を基準として5mol 1%以上であることが好ましく、10mol 1%以上であることがより好ましく、15mol 1%以上であることが更に好ましい。水酸基を有する有機オニウム塩の配合割合が5mol 1%未満であると、ポリ乳酸又はその重合性単量体(乳酸、ラクチド)との親和性が不十分となり、これらが層状化合物の層間に安定的に保持されにくくなる傾向にある。

【0039】本発明の生分解性樹脂複合材料において、ポリ乳酸と有機化された層状粘土鉱物との含有比率は、前者100重量部に対して後者が好ましくは0.5~30重量部であり、より好ましくは1~20重量部である。層状粘土鉱物の含有量が前記下限値未満であると、剛性及び結晶化速度の向上の程度が不十分となる傾向にあり、他方、前記上限値を超える場合には、ポリ乳酸が連続層を形成できなくなる傾向にあり、生分解性樹脂複合材料の剛性が低下する恐れがある。

【0040】また、本発明の生分解性樹脂複合材料に含まれる層状化合物の層間距離は、各層の重心間の平均距

離を基準として5nm以上であることが好ましく、10nm以上であることがより好ましい。層状化合物の層間距離が5nm未満であると、ポリ乳酸の分散性が不十分となる傾向にある。

【0041】次に、本発明の生分解性樹脂複合材料の第1及び第2の製造方法について説明する。

【0042】本発明の第1の製造方法は、水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、有機化工程で得られる層状粘土鉱物とポリ乳酸とを溶融混練し、有機オニウム塩の水酸基とポリ乳酸の末端カルボキシル基とを反応させる溶融混練工程とを含むものである。

【0043】有機化工程は、例えば本出願人により特許第2627194号公報に開示されている方法により行うことができる。すなわち、層状粘土鉱物中の無機イオンを、水酸基を有する有機オニウム塩から生じる有機オニウムイオン(例えば有機アンモニウム塩においては有機アンモニウムイオン)によりイオン交換することによって、層状粘土鉱物の有機化を行うことができる。

【0044】より具体的には、例えば水酸基を有する有機アンモニウム塩を用いる場合には、次のような方法により有機化を行うことができる。すなわち、塊状の層状粘土鉱物を用いる場合は、先ずこれをポールミル等により粉碎し粉体化する。次いで、ミキサー等を用いてこの粉体を水中に分散させ層状粘土鉱物の水分散物を得る。これとは別に、水酸基を有する有機アミン及び塩酸等の酸を水に加えて、水酸基を有する有機アンモニウム塩の水溶液を調整する。この水溶液を上記層状粘土鉱物の水分散物に加え混同することにより、層状粘土鉱物中の無機イオンが有機アンモニウム塩から生じた水酸基を有する有機アンモニウムイオンによりイオン交換される。この混合物から水を除去することにより有機化された層状粘土鉱物を得ることができる。

【0045】有機アンモニウム塩や層状粘土鉱物の分散媒体としては、水以外にもメタノール、エタノール、プロピルアルコール、イソブロパノール、エチレングリコール及びこれらの混合物、並びにこれらと水との混合物を使用することができる。

【0046】かかる有機化工程においては、水酸基を有さない有機オニウム塩(例えば上記一般式(4)で表される有機アンモニウム塩)で層状粘土鉱物を更に有機化してもよいが、第1の製造方法では、これらの2種の有機オニウム塩による共有機化を行わなくとも、層状粘土鉱物の分散均一性を高水準に維持しつつその添加量を増加することができる。なお、水酸基を有さない有機オニウム塩での有機化は、水酸基を有する有機オニウム塩での有機化と同時にあってもよく、水酸基を有する有機オニウム塩での有機化の後に行なってよい。

【0047】次に、溶融混練工程において、有機化工程で得られる層状粘土鉱物とポリ乳酸とを溶融混練し、有

機オニウム塩の水酸基とポリ乳酸の末端カルボキシル基とを反応させることによって、本発明の生分解性樹脂組成物が得られる。

【0048】混練工程における温度は、有機オニウム塩の水酸基とポリ乳酸の末端カルボキシル基とが反応可能であれば特に制限されないが、好ましくは150～250℃である。当該温度が前記下限値未満であると、ポリ乳酸の溶融が不十分となり、層状粘土鉱物をポリ乳酸中に均一に分散させにくくなる傾向にある。また、当該温度が前記上限値を超えると、ポリ乳酸の分子量が低下して樹脂複合材料の物性が損なわれる（例えば可塑化）傾向にある。

【0049】また、混練工程の際には、本出願人により国際公開WO99/50340号公報に開示されている方法に準じて行うことが好ましい。すなわち、高樹脂換算圧力、高総せん断量、高せん断エネルギーを加えることが可能なスクリューを備える二軸混練機を用い、樹脂換算圧力の平均値が $5 \times 10^4 \text{ Pa}$ 以上、最大値が $1 \times 10^5 \text{ Pa}$ 、総せん断量が $10^5 \sim 10^7$ 、総せん断エネルギーが $10^{10} \sim 10^{14} \text{ Pa}$ の条件下で有機化された層状粘土鉱物とポリ乳酸とを溶融混練することによって、層状粘土鉱物をポリ乳酸中に均一に微分散することができる。

【0050】本発明の第2の製造方法は、水酸基を有する有機オニウム塩で層状粘土鉱物を有機化する有機化工程と、有機化工程で得られる層状粘土鉱物と、L-乳酸、D-乳酸、L-ラクチド、D-ラクチド及びmeso-ラクチドからなる群より選ばれる少なくとも1種の重合性単量体とを混合し、前記有機オニウム塩の水酸基を反応点として前記重合性単量体を重合させてポリ乳酸を生成させる重合工程とを含むものである。

【0051】第2の製造方法にかかる有機化工程は、上記した第1の製造方法にかかる有機化工程と同様にして行うことができる。また、第2の製造方法にかかる有機化工程においても、水酸基を有さない有機オニウム塩（例えば上記一般式（4）で表される有機アンモニウム塩）で層状粘土鉱物を更に有機化することが好ましい。これにより、後述する重合工程において、層状粘土鉱物の分散均一性を高水準に維持しつつその添加量を増加することができる。更に、これら2つの有機オニウム塩の含有比率を適宜選択することによって、層状粘土鉱物の層間及び/又は表面における水酸基の存在割合を制御し、生成するポリ乳酸の分子量を調整することができる。ポリ乳酸の分子量を低下させずに層状粘土鉱物の添加量を増加することができる。なお、水酸基を有さない有機オニウム塩での有機化は、水酸基を有する有機オニウム塩での有機化と同時にあってもよく、水酸基を有する有機オニウム塩での有機化の後に行つてもよい。

【0052】次に、重合工程において、有機化工程で得られる層状粘土鉱物と、L-乳酸、D-乳酸、L-ラク

チド及びD-ラクチドからなる群より選ばれる少なくとも1種の重合性単量体とを混合し、前記有機オニウム塩の水酸基を反応点として前記重合性単量体を重合させることによって、ポリ乳酸が生成する。ここで、L-乳酸及び/又はD-乳酸を用いる場合にはこれらの直接重縮合によりポリ乳酸が生成し、他方、L-ラクチド及び/又はD-ラクチドを用いる場合にはこれらの開環重合によりポリ乳酸が生成する。これらの重合は、所定の触媒を用いて行ってもよく、無触媒下で行ってもよい。触媒としては、具体的には、オクチル酸スズ、塩化スズ、塩化亜鉛、酸化鉛、炭酸鉛、塩化チタン、アルコキシチタン、酸化ゲルマニウム、酸化ジルコニウムなどが挙げられ、その使用量は重合性単量体100重量部に対して0.001～1重量部であることが好ましい。また、重合工程における反応温度は100～200℃であることが好ましい。

【0053】このように、本発明の第1及び第2の製造方法はいずれもポリ乳酸と層状粘土鉱物との間に有機オニウム塩の水酸基を介した結合を形成させるもので、これにより、層状粘土鉱物がポリ乳酸中に十分に均一に分散され、優れた剛性と十分に高い結晶加速度とを有する本発明の生分解性樹脂を効率よく且つ確実に得ることができる。

【0054】

【実施例】以下、実施例及び比較例に基づいて本発明を更に具体的に説明するが、本発明は以下の実施例に何ら限定されるものではない。

【0055】実施例1

（層状粘土鉱物の有機化）ナトリウム型モンモリロナイト（クニミネ鉱業製クニピアF、陽イオン交換容量：1.15 meq/100g）100gを80℃の水5000mlに分散させ、一方、ジヒドロキシエチルメチルステアリルアンモニウムプロミド59.2gを80℃の水2000mlに溶解させた後、両者を混合してモンモリロナイトの有機化を行った。得られた有機化モンモリロナイト（以下、 $18(\text{OH})_2\text{-Mont}$ という）を80℃の水で3回洗浄し、凍結乾燥した後、これを粉碎した。灼残法により求めた $18(\text{OH})_2\text{-Mont}$ の無機分の残量は63%であった。

【0056】（層状粘土鉱物とポリ乳酸との混練）スクリューを備える二軸押出機（日本製鋼所製TEX30α）を用い、ポリ乳酸樹脂（島津製作所製ラクティ#9030）に $18(\text{OH})_2\text{-Mont}$ を無機分換算値で3重量%添加した混合物を、スクリュー回転数300 rpm、樹脂温度200℃、樹脂供給速度5kg/hで溶融混練し、目的の樹脂複合材料を得た。得られた樹脂複合材料をストランド状に押し出した後、水で急冷し、ストランドカッターでペレットとした。

【0057】（分散状態の評価）上記のペレットをミクロトームで切り出して超薄切片を作製した。これを透過

型電子顕微鏡（日本電子製 J O E L - 2 0 0 C X ）で観察し、層状粘土鉱物の分散状態を以下の基準：

○：層状粘土鉱物がほぼ単層ごとに微分散している
 △：2～3層が凝集した状態の層状粘土鉱物が50%以上認められる
 ×：ほとんどの層状粘土鉱物が数十層以上凝集した状態で分散している

に基づいて評価した。得られた結果を表1に示す。

【0058】（剛性の評価）射出成形機（日精樹脂工業製P S 4 0 E 2 A S E ）及びF S 7 5型を用いて上記の樹脂複合材料の射出成形を行い、ダンベル型引張試験片を得た。この試験片を用い、A S T M D 6 3 8 Mに準じて引張り試験を行い、引張強さ、破断伸び、弾性率を評価した。また、A S T M D 2 5 6に準じてI z o d衝撃試験を行った。得られた結果を表1に示す。

【0059】（結晶化時間の測定）上記のペレットを用い、D S C測定装置（パーキンエルマー社製D S C-7）により結晶化時間を測定した。すなわち、試料0.3m gをアルミパンに入れ、200℃で5分間保持してから110℃まで急激に降温して保持し、降温してから結晶化の吸熱ピークが現れるまでの時間を結晶化時間とした。得られた結果を表1に示す。

【0060】実施例2

ジヒドロキシエチルメチルステアリルアンモニウム塩の代わりに、ジヒドロキシエチルメチルアルキルアンモニウム塩（花王製アミート102、アルキル：ヤシ油由来のアルキル基、組成：オクチル/デシル/ドデシル/テトラデシル/オクタデシル/オレイル=7/7/51/19/8/2/6）を用いてモンモリロナイトの有機化を行い、得られた有機化モンモリロナイト（A 1 0 2 - M o n t ）を使用したこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表1に示す。

【0061】実施例3

先ず、実施例1と同様にして18(OH)₂-M o n tを合成した。次に、L-ラクチド100g、18(OH)₂-M o n t 3.5g、オクチル酸スズ200m gを反応容器に入れ、10⁻²mmHgまで減圧した。統いて十分攪拌しながら徐々に温度を上昇させ、160℃で3時間保持した。反応生成物をクロロホルムに溶解し、メタノール中に滴下して樹脂複合材料を単離精製した。*

12
 *【0062】得られた樹脂複合材料について、実施例1と同様にして、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表1に示す。

【0063】実施例4

18(OH)₂-M o n tの代わりに、(CH₃CH₂)₃N⁺(CH₂)₁₁OHBr⁻で有機化したモンモリロナイト(11OH-M o n t)を用いたこと以外は実施例3と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表1に示す。

【0064】実施例5

18(OH)₂-M o n tの代わりに、ジヒドロキシエチルステアリルアンモニウム塩とトリメチルステアリルアンモニウム塩との混合物（モル比7:3）で有機化したモンモリロナイト(OH/C18-M o n t)を用いたこと以外は実施例3と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表1に示す。

【0065】比較例1

20ポリ乳酸を単独で用い、実施例1と同様にして、剛性の評価及び結晶化時間の測定を行った。得られた結果を表2に示す。

【0066】比較例2

18(OH)₂-M o n tの代わりに、12-アミノドデカン酸で有機化したモンモリロナイト(12COOH-M o n t)を用いたこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表2に示す。

【0067】比較例3

3018(OH)₂-M o n tの代わりに、ステアリルトリメチルアンモニウムで有機化したモンモリロナイト(C18Me₃-M o n t)を用いたこと以外は実施例1と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表2に示す。

【0068】比較例4

18(OH)₂-M o n tの代わりに12COOH-M o n tを用いたこと以外は実施例3と同様にして、樹脂複合材料を作製し、分散状態及び剛性の評価並びに結晶化時間の測定を行った。得られた結果を表2に示す。

【0069】

【表1】

	実施例1	実施例2	実施例3	実施例4	実施例5
分散状態	○	○	○	○	○
引張強さ[MPa]	72.4	70.4	71.9	70.8	70.0
引張破断伸び[%]	5.2	5.4	5.1	5.6	4.9
引張弾性率[GPa]	1.65	1.62	1.64	1.62	1.64
Izod衝撃値[J/m]	23.8	25.0	24.1	23.5	22.9
結晶化時間[min]	5.3	10.5	5.0	6.1	6.9

分散状態	比較例1	比較例2	比較例3	比較例4
分散状態	-	×	×	△
引張強さ [MPa]	61.2	45.3	58.0	58.5
引張破断伸び[%]	8.4	1.5	2.8	3.1
引張弾性率 [GPa]	1.31	1.52	1.58	1.58
Izod衝撃値 [J/m]	26.6	12.2	18.2	18.8
結晶化時間 [min]	54.5	42.2	35.5	32.7

【0071】表1に示すように、実施例1～5の樹脂複合材料では、いずれも層状粘土鉱物がポリ乳酸中に微細に分散しており、ポリ乳酸単独（比較例1）の場合に比べて剛性及び結晶化速度の向上が認められた。

【0072】一方、表2に示すように、比較例2～4の樹脂複合材料では、層状粘土鉱物が凝集したままポリ乳酸中に分散しており、単に硬く脆い材料であることがわかった。

【0073】

【発明の効果】以上説明した通り、本発明の樹脂複合材料では、水酸基を有する有機オニウム塩で層状粘土鉱物*

*を有機化し、該有機オニウム塩の水酸基を介してポリ乳酸と層状粘土鉱物とを結合させることによって、有機オニウム塩により広げられた層状粘土鉱物の層間にポリ乳酸が安定的に保持されるので、層状粘土鉱物をポリ乳酸中に十分に均一に分散させることができる。その結果、優れた剛性と十分に高い結晶化速度とを達成することができる。

【0074】また、本発明の樹脂複合材料の製造方法によれば、このように優れた特性を有する本発明の樹脂複合材料を効率よく且つ確実に得ることができる。

フロントページの続き

(72)発明者 月ヶ瀬 あづさ

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内

(72)発明者 白井 有光

愛知県愛知郡長久手町大字長湫字横道41番
地の1 株式会社豊田中央研究所内
F ターム(参考) 4J002 CF181 CF191 DJ006 FB086
FD016
4J029 AA02 AB05 AC01 AD10 EA05
EH03 KJ08